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(54) **Composition particularly for use as an ocular membrane and a method for the preparation of an ocular membrane**

(57) A composition suitable for use in an ocular membrane is selected from copolymers and terpolymers of an addition cross-linked polysiloxane and one or more glycol mono- or di- or ether-esters of acrylic or methacrylic acid in proportions such that the compositions when used in ocular membranes worn in contact with the eye possess the necessary oxygen permeability, light transmission, wettability, mucophobicity and lipophobicity, but are not water-swellable.

A method of preparing such an ocular membrane comprises placing the composition between disposable moulds and curing it therein. The cured, mechanically and optically finished ocular membrane is recovered by the destruction of the moulds without secondary operations.

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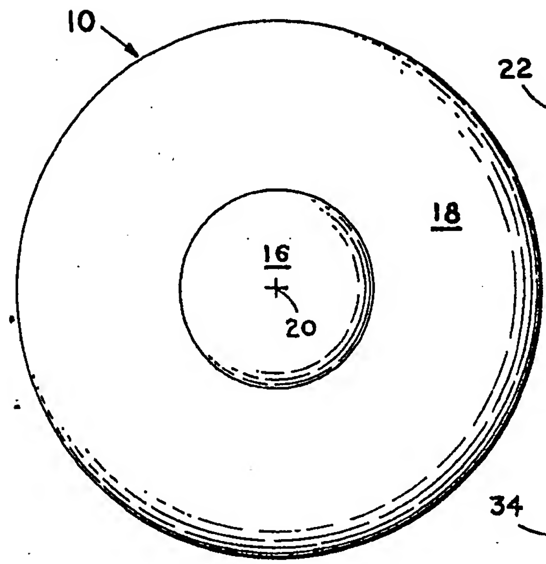

FIG. 1

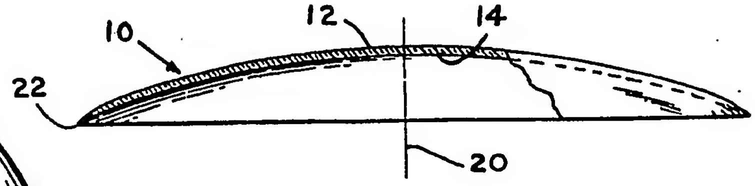

FIG. 2

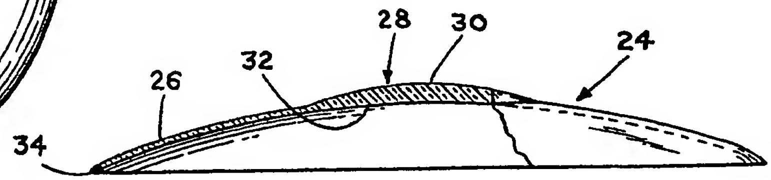

FIG. 3

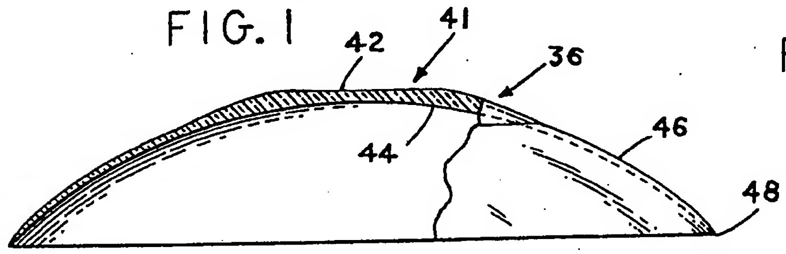

FIG. 4

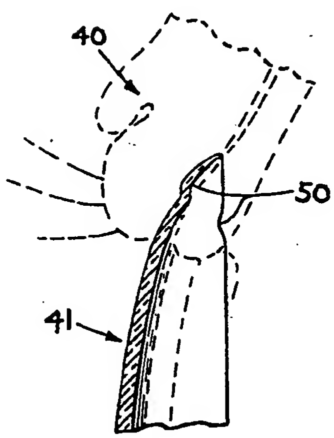

FIG. 5a

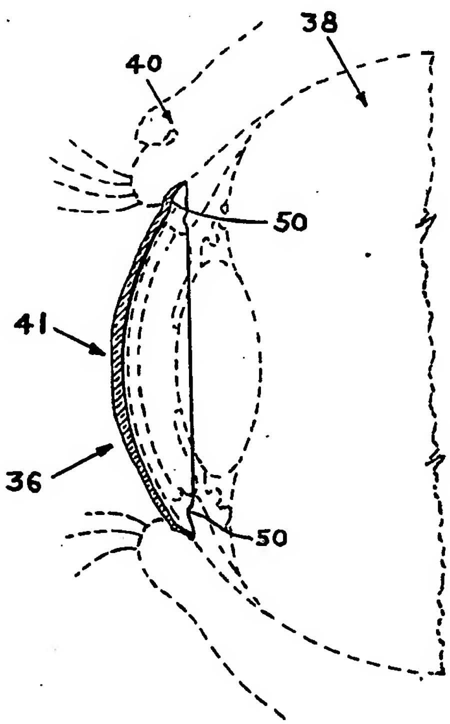

FIG. 5

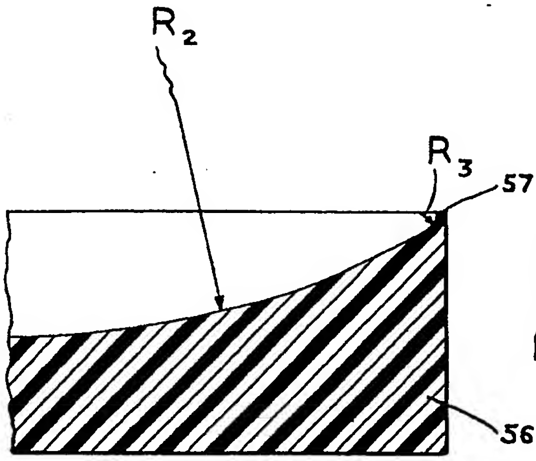

FIG. 7

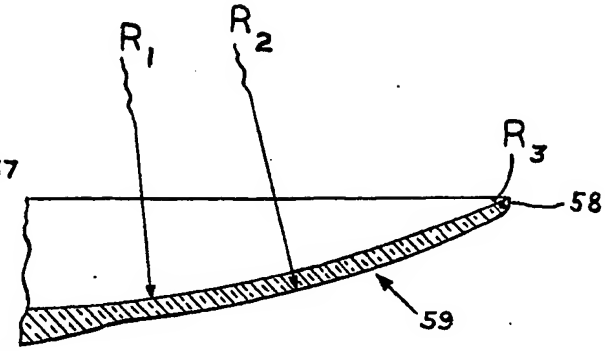

FIG. 8

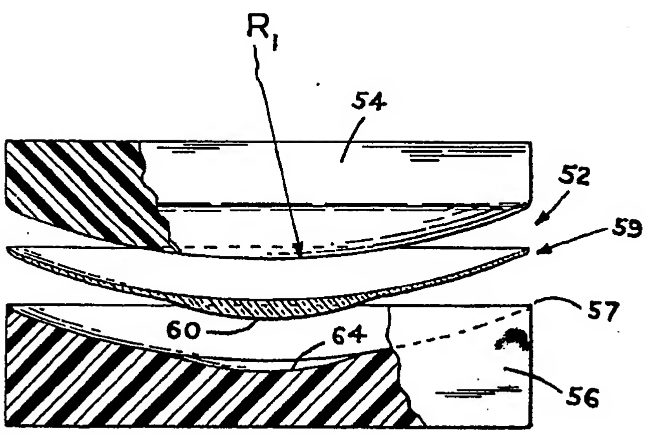

FIG. 6

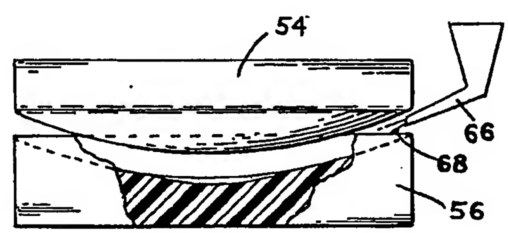

FIG. 9

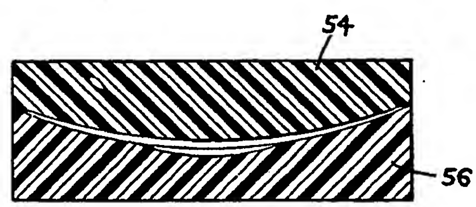

FIG. 10

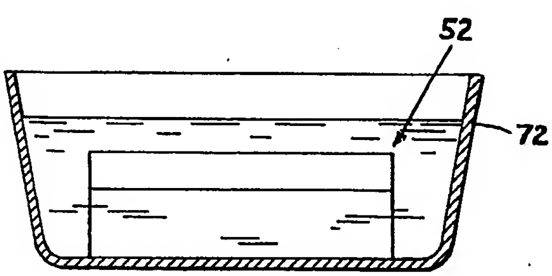

FIG. 11

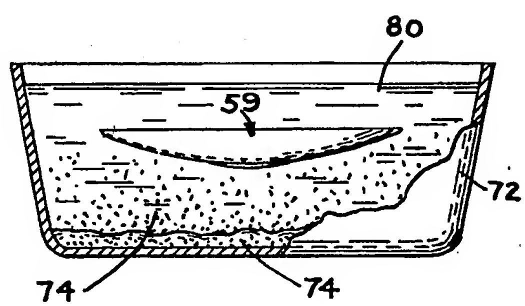

FIG. 12

SPECIFICATION

Compositi n particularly for use as an ocular membran and a method for the preparation of an ocular membrane

This invention relates to a composition particularly for use as an ocular membrane and to a method for the preparation of an ocular membrane. More particularly, the invention relates to a disposable, thin membrane formed for ocular and other therapeutic use from the aforementioned composition, which membranes can be worn for long periods of time without discomfort.

Optical contact lenses are conventionally made of either hard plastics, such as acrylic resins or materials which are hydrophilic and water swellable (the so-called "soft" lenses). The resins utilized conventionally must, of course, possess the various properties required for ophthalmic use with respect to for example their light transmission and durability. However, all of the known lenses have the basic defect that they cannot be worn regularly in the eye for a long period of time, i.e. for more than about fourteen to eighteen hours. Most certainly, their use is not recommended during sleep. Consequently, the contact lenses known to date should be inserted and removed daily from the eye.

Furthermore, those "hard" lenses made from polymethylmethacrylate resins possess excellent rigidity and durability for handling by the user. However, they are highly impermeable to oxygen and carbon dioxide, which are necessary for the proper metabolic functioning of the eye. These resins are also hydrophobic and as a result lack surface wettability.

The so-called "soft" lenses which are water swellable and hydrophilic must be maintained under conditions of sterility. This results in various inconveniences to the user.

Moreover, the "soft" lenses which are made from water swellable, hydrophilic polymers do not have the durability of the "hard" acrylic resin materials and are much more difficult to handle. Further, they are water swellable and can absorb an amount of water which is equal to many times the original volume of the lens. Consequently, the dimensions of such lenses are constantly undergoing change, which, in turn, changes the refractive index, and the refractive or ophthalmic properties of the lens.

Also, when such lenses are manufactured in the dry, unswollen state, the ultimate dimensions of the lens can vary greatly because minor deviations from standards will be amplified many times when the lens fully swells. Therefore, the manufacture of "soft" lenses to the exacting tolerances required is relatively difficult, as is repetitive production or duplication of lenses of the same refraction and curvative parameters.

An additional problem with such contact lenses is that the cornea, which the lens rests on or covers, must have an adequate supply of oxygen, much of which is supplied by the tear fluid which bathes the cornea. This oxygen, presumably from the atmosphere, dissolves in the tear fluid and it is this dissolved oxygen which is then transferred to the cornea.

The so-called "soft" lenses, like "hard" lenses, do not possess satisfactory permeability to oxygen and consequently offer no solution to this problem.

Attempts have been made to use a polysiloxane gum as a contact lens because of its high permeability to oxygen (see, for example, U. S. Patent No. 3,228,741). However, this particular material is quite hydrophobic. In order to ensure proper comfort and wearability in a contact lens or material that is in direct contact with the eye, it is important that the material be wettable, i.e. so that the tear fluid will form a continuous film on the lens and not bead up. In use, this film is renewed at each eyelid blink so that, as a practical matter, the material must have sufficient wettability to allow formation of a continuous film of tear liquid, which film will last for the duration of the blink period.

The cross-linked polysiloxanes do not possess this property and have thus found little use in the contact lens field.

Another problem with the siloxane materials is that, when placed in the eye, the surfaces of the lens attract ocular debris, e.g. proteins, lipids, mucoids, which the eye is constantly giving off. One of the functions of the tear liquid is to wash away this debris. However, the polysiloxane material is lipophilic and mucophilic, i.e. attracts this ocular debris, and this further restricts the siloxane material for ophthalmic use.

Attempts have also been made to modify such polysiloxanes by grafting, i.e. coating the surface thereof with another type of polymer. Such attempts have been generally unsuccessful because of the difficult techniques involved in obtaining lenses and optically acceptable membranes from such non-uniform systems.

In my British Patent Application No. 48502/78, I have disclosed a polysiloxane copolymer composition which possesses a number of properties which make it highly suitable for use as an ocular lens, among which are excellent wettability and oxygen permeability. Additionally, the composition disclosed therein allows for the accurate reproduction of tolerances and lens parameters.

The present invention in one aspect provides a composition comprising a uniform polymer selected from copolymers and terpolymers of an addition cross-linked polysiloxan and one or more esters having the formula:

$$A-\overset{\overset{\displaystyle O}{\|}}{C}-O(CR'_2)_x-\left[\begin{matrix}CH_3\\ |\\ C\\ |\\ CH_3\end{matrix}\right]_y-(CR'_2)_zO-R \qquad (I)$$

wherein:

A is $CH_2{=}CH-$ or $CH_2{=}\overset{\overset{CH_3}{|}}{C}-$,

R' may be the same or different in each occurrence and is hydrogen or methyl,

R is hydrogen, an alkyl group having one of three carbons atoms,

$CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}$, or $CH_2{-}\overset{\overset{CH_3}{|}}{C}{-}\overset{\overset{O}{\|}}{C}$,

x and z are each integers from 0 to 4,

y is 0 or 1,

the sum of x and z is one or more, and when y is 1 x and z are equal,

the amount of the ester in the polymer being effective to provide the composition with sufficient light transmission, liphobicity, mucophobicity, and surface wettability, for wearing in contact with the human eye but less than that which would make the composition water swellable.

The invention in another aspect provides an ocular membrane formed from a composition according to the first aspect of the invention.

Thus there is provided a polymeric composition which is suitable for making an ocular membrane which possesses excellent optical properties and excellent permeability to oxygen and carbon dioxide. The material is hydrophobic, in other words essentially non-water swellable. However, the surface of the material is highly wettable, i.e. allows a continuous tear liquid film to be formed and maintained during the normal blink period.

Additionally, the polymer composition of the present invention possesses all of the desirable properties of the composition disclosed in the above-mentioned British Patent Application No. 48502/78.

As a result of all these properties, this composition can be used to make thin ocular membranes which, after initial insertion of the eye, can be worn for extended periods, for example for several days to several months, and need not be removed daily from the eye.

Also, the membrane made from the present invention can be used as an ocular bandage or therapeutic device.

By uniform, it is meant that the entire composition, and more particularly an ocular membrane made from the composition, is chemically homogenous and not composed of layers or coatings of one type of polymer on the surface of another polymer.

The amount of the total ester in the polymer composition is that amount which is sufficient to impart wettability to the surface of articles formed from the composition but which is below that amount which would make the composition water swellable. As used herein, the term "wettability" means that the surface of the material should have the ability to allow the formation of a continuous film of tear liquid across the surface of the material and the maintenance of the film, without intermittent beading up, for the normal period of the blink cycle. In this regard, it is noted that this particular property is best determined from empirical measurements on the eye of humans. In practice, if the material wets too poorly for use as a lens or therapeutic ophthalmic device, e.g. a bandage, it will be immediately evident to the clinical observer. The material is "water swellable" if it absorbs more than about 10% by weight of water.

Ocular membranes made from this composition are highly permeable to oxygen and carbon dioxide, which are necessary for proper metabolic functioning of the eye. The lens material is inert and non-toxic and completely compatible with the natural precorneal fluid. It also possesses excellent stability with respect to the index of refraction and light transmission on the eye and thus does not cause variations in visual acuity.

Of significant importance is that the polymeric composition of the present invention, while possessing the desirable properties of the polysiloxane, namely the higher oxygen and carbon dioxide permeability, also avoids the mucophilicity and lipophilicity of the polysiloxane. Thus, lenses and bandages composed of the composition stay clean and free of ocular protein debris for extended periods of time while worn on the eye.

The invention in a further aspect provides a method of forming an ocular membrane, comprising forming ophthalmically contoured concave and convex mould members adapted to mutually engage along a continuous closed loop; introducing into the said concave mould member a polymerizable material comprising an addition cross-linkable polysiloxane and one or more esters having the formula:

$$A{-}\overset{\overset{O}{\|}}{C}{-}O(CR'_2)_x{-}\left[\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\right]_y{-}(CR'_2)_zO{-}R \qquad (I)$$

wherein:

A is $CH_2{=}CH-$ or $CH_2{=}\overset{\overset{CH_3}{|}}{C}-$,

R' may be the same or different in each occurrence and is hydrogen or methyl,

R is hydrogen, an alkyl group having one to three carbon atoms,

$CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}$, or $CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}\overset{O}{\overset{\|}{C}}$,
x and z are integers from 0 to 4,
y is 0 or 1,
the sum of x and z is one or more, and when y is 1 x and z are equal,

the amount of the ester in the polymer being effective to provide the composition with sufficient light transmission, liphobicity, mucophobicity, and surface wettability, for wearing in contact with the human eye but less than that which would make the composition water swellable; contacting the convex mould member with the concave mould member to expel excess polmerizable material therefrom and to form a substantially closed mould chamber having essentially the size and shape of the completed membrane; subjecting the thus-introduced polymerizable material to polymerization conditions to form a polymeric ocular membane from the said material possessing the contours of the substantially closed mould chamber; and freeing the formed ocular membrane from the substantially closed mould chamber.

Because of the complete interfacing of the cured membrane and the mould surfaces, freeing of the cured membrane from the mould surfaces without damage to the cured membrane is best accomplished by destruction of the mould surfaces, although other methods of removal can be used. What is important, however, is that the method of the present invention allows for the exact replication of less parameters, which is difficult or impossible to obtain with the "soft" lenses. Further, ocular membranes can be produced by the method of the present invention in final form in closed moulds without being encumbered by flashings or the need for edging.

An ocular membrane is prepared by the method of the present invention by introducing an uncured composition according to the first aspect of the invention into an ophthalmically contoured mould chamber formed from concave and convex mould members. The mould members form a substantially closed mould chamber. The mould members are preferably formed from a material which is highly soluble in a given solvent, which solvent is a non-solvent for the cured membrane polymer. Then the composition in the mould chamber is subjected to curing.

In another approach, the mould members may be formed of a material which melts at a temperature which is non-injurious to the cured membrane polymer composition.

Alternatively, the mould members may be made from a material which may be destroyed by acid, base or reagents which are non-injurious to the cured membrane polymer composition.

The invention will be further described, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is a top plan view of an ocular membrane made in accordance with the present invention;

Figures 2-4 are partial cross-sectional views of ocular membranes made in accordance with the present invention;

Figure 5 shows an ocular membrane made in accordance with the present invention in position when operatively placed on the human eye;

Figure 5a is an enlarged view of a portion of Figure 5;

Figure 6 shows a cured ocular membrane in relation to mould surfaces used in its formation;

Figure 7 is an enlarged view of a portion of the mould shown in Figure 6;

Figure 8 is an enlarged view of a portion of the ocular membrane shown in Figure 6; and

Figures 9-12 depict sequential steps in the method of the present invention.

The first component of the composition of the present invention is a cross linkable polysiloxane or "flexible silicon resin" which, because of availability, is usually a dimethylpolysiloxane polymer. Such dimethylpolysiloxanes are well known in the art and methods for the preparation of such materials are well known. Typical siloxane polymers and methods for their preparation are described in detail in United States Patent No. 2 560 498.

A typical polysiloxane which can be used in the present invention is dimethylpolysiloxane wherein up to about one per cent of the methyl groups are substituted with vinyl groups. To cross-link the dimethylpolysiloxane, polymethylhydrogen siloxane can be used wherein one of the methyl groups of the dimethylpolysiloxane is substituted with hydrogen. Each of these polymers is well known and commercially available.

The molecular weight or viscosity of the polysiloxane is not critical. Of course, the viscosity of the polysiloxane must be such that it forms a pourable liquid suitable for introduction into the mould members used in the preparation of ocular membranes.

As is known, dimethylpolysiloxanes can be cured or cross-linked by either condensation or addition polymerization. However, in the present case, addition polymerization is us d since the water which is produced with condensation polymerization causes non-uniformities in the final polymer due to the escape of the water from the reaction. Also, the water which does not escape results in the formation of bubbles or voids in the final product. The presence of this water renders the light transmission of the final composition unsuitable for ocular use.

Typical addition cross-linking polymerizations are disclosed in United States Patent No. 2 970 150. It is also well known to include fillers such as silica in such polysiloxane materials, and their use in the composition is

suitable so long as the fill rs do not interfere with the desired properties of the final membrane. Typically, for example up t 50% by weight f fine powd red silica can be used for reinforcem nt of the polysiloxane.

Such polysiloxanes are cross-linked to form elastomers by the use of a suitable cross-linking catalyst, which catalysts are also well known (see, for example, United States Patent No. 2 823 218). A typical catalyst is chlorplatinic acid, although many other perfectly satisfactory cross-linking catalysts are well known and are readily available commercially.

The addition cross-linked elastomers formed from the resin systems are extremely hydrophobic. Thus, they are not suitable for use as a contact lens, although they possess the transparency, mechanical strength, durability and dimensional stability required.

Consequently, in the present invention, the resin is copolymerized with one or more esters having the formula (I). The total amount of the ester which is used in the final elastomeric polymer composition is that amount which is effective to impart wettability to the surface of an article formed therefrom, for example an ocular membrane, but in an amount less than that which would make the composition water swellable.

The esters which can be used to form a copolymer or terpolymer in conjunction with the polysiloxane are those formed from the reaction of acrylic or methacrylic acid and can be appropriate straight chained or branched alcohols. Methods for carrying out the esterification reaction are well known in the art, see for example F. W. Billmeyer, *Textbook of Polymer Science,* Interscience Publisher, 5th Ed., 1970, pp. 403, and such esters are available commercially; see also Morrison & Boyd, *Organic Chemistry,* Allyn & Bacon, Inc., First Ed., pages 152, 153 and 650-675.

These esters may be either the mono or diesters of the acrylic acids and have the formula (I) alone. Esters, their precursor alcohols and respective structural formulas which are particularly suitable for use in the present invention are as follows:

TABLE 1

Precursor Alcohol	Ester No.	Ester (mono or diester with acrylic or methacrylic acid)
Propylene glycol (1,2 Propanediol) $CH_3H\ OH\ CH_2\ OH$	1	2-hydroxy propyl methacrylate (Propylene Glycol mono methacrylate) O $CH_2{=}CCOCHCH_2OH$ CH_3 CH_3
Bytylene glycol $HOCH_2CH_2CH_2CH_2OH$	2	1,4, Butylene glycol monomethacrylate O $CH_2{=}CC{-}OCH_2CH_2CH_2CH_2OH$ CH_3
Hexamethylene glycol (1, 6 Hexanediol) $HOCH_2CH_2CH_2CH_2CH_2CH_2OH$	3	Hexamethylene glycol diacrylate O O $CH_2{=}CHCOCH_2CH_2CH_2CH_2CH_2CH_2OCCH{=}CH_2$
Hexamthylene glycol (1, 6 Hexanediol) $HO[CH_2]_6OH$	4	Hexamethylene glycol dimethacrylate O O $CH_2{=}C\ C\ OCH_2CH_2CH_2CH_2CH_2CH_2O\ C\ C{=}CH_2$ CH_3 CH_3

TABLE I (cont...)

Precursor alcohol	Ester No.	Ester (mono or diester with acrylic or methacrylic acid)
Ethylene glycol monomethyl ether (2-Methoxy ethanol) $CH_3OCH_2CH_2OH$	5	2-Methoxy ethyl methacrylate $CH_2{=}\underset{CH_3}{C}\overset{O}{\overset{\parallel}{C}}OCH_2CH_2OCH_3$
Ethylene glycol monomethyl ether (2-Methoxy Ethanol) $CH_3OCH_2CH_2OH$	6	2-Methoxy ethyl acrylate $CH_2{=}CH\overset{O}{\overset{\parallel}{C}}OCH_2CH_2OCH_3$
Tetramethylene glycol (1, 4 Butanediol) $CH_2OHCH_2CH_2CH_2OH$	7	Tetramethylene glycol diacrylate $CH_2{=}CH\overset{O}{\overset{\parallel}{C}}OCH_2CH_2CH_2CH_2O\overset{O}{\overset{\parallel}{C}}CH{=}CH_2$
Tetramethylene glycol (1, 4 Butanediol) $CH_2OHCH_2CH_2CH_2OH$	8	Tetramethltene glycol dimethacrylate $CH_2{=}\underset{CH_3}{C}\overset{O}{\overset{\parallel}{C}}OCH_2CH_2CH_2CH_2O\overset{O}{\overset{\parallel}{C}}\underset{CH_3}{C}{=}CH_2$
Neopentyl gylcol (2, 2 Dimethyl, 1, 3 Propanediol) $HOCH_2C(CH_3)_2CCH_2OH$	9	Neopentyl glycol diacrylate $CH_2{=}CH\overset{O}{\overset{\parallel}{C}}—OCH_2\underset{CH_3}{\overset{CH_3}{C}}CH_2O—\overset{O}{\overset{\parallel}{C}}CH{=}CH_2$
Neopentyl glycol (2, 2 Dimethyl, 1, 3 Propanediol) $HOCH_2—\underset{CH_3}{\overset{CH_3}{C}}—CH_2OH$	10	Neopentyl glycol dimethacrylate $CH_2{=}\underset{CH_3}{C}\overset{O}{\overset{\parallel}{C}}OCH_2\underset{CH_3}{\overset{CH_3}{C}}CH_2O\overset{O}{\overset{\parallel}{C}}\underset{CH_3}{C}{=}CH_2$

The above not d esters may be used singularly as the est r component of a copolym r of the present invention. Additionally, any two of thes esters may be used as the two est r components of a terpolymer of the present invention.

Particularly preferred esters for the copolymer and terpolymer combinations are:

(a) 2-methoxyethylacrylate;
(b) propylene glycol monomethyacrylate and tetramethylene glycol diacrylate(terpolymer);
(c) hexamethylene glycol diacrylate;
(d) propylene glycol monomethacrylate;

(e) neopentyl glycol dimethacrylate; and
(f) 1,4 butylene glycol monomethacrylate.

Of course, the esters may be used int rchangeably to vary the desired properti s of the final composition or to facilitate processing.

More particularly, any one of the individual esters may be polymerized with the polysiloxane to form a copolym r in accordance with the present invention. The amount of such ester is generally from 0.2 to 5.0 per cent by weight of the total polymer. However, the specific amount of ester used is determined by the ultimate properties desired, e.g. light transmission, wettability.

Alternatively, two of the esters may be polymerized with the polysiloxane to form a terpolymer. In this case, the amount of the individual esters may also be varied to modify the properties as desired. Again, however, the total amount of the esters in the terpolymer is generally from 0.2 to 5 per cent by weight. With these materials, it is possible to achieve varying degrees of surface wettability, lipo- and muco-phobicity, and transparency, depending on the final values for these properties which are required in the end product.

As used herein the term "wettability" means that the surface of optical membranes or contact lenses formed from the composition wet sufficiently so as to maintain uninterrupted refractive functioning. The "wettability" of membranes in accordance with the present invention is difficult to quantify because the wettability properties which are required must be present when the membrane is in contact with the eye, which situation cannot be practicably duplicated for the purposes of laboratory measurement. Fortunately, however, the "wettability" can be easily determined from empirical clinical observation.

Atempts have been made to simulate the *in vivo* environment under which contact lenses function so as to measure the so-called "contact angle" of the surface of a given material and thus evaluate its potential performance. The most recent evaluative procedure is reported in *International Contact Lens Clinic*, Volume 5, No. 1, January-February, 1978, in an article entitled "Measuring the Contact Lens Wetting Angle in a Simulated *in vivo* Environment" (herein referred to as the "*in vivo*" method). As measured by this method, the composition of the present invention in the fully hydrated state exhibits contact angles of up to 30°, with a mean value of about 18°.

At the same time, however, the composition must not be rendered so hydrophilic as to absorb significant amounts of water, i.e. more than 10% by weight. As noted hereinabove, this is one of the basic disadvantages of the so-called "soft" lenses now in use. As used herein, the expression "hydrophilic" means that the composition does absorb significant amounts of water.

The phenomenon of such hydrophilicity or swellability is to be distinguished from the property of "water permeability", the latter property being possessed by the compositions of the present invention. The term "water permeability" as used herein means that the composition permits water to pass through the membrane without any appreciable retention of the water within the composition. This property is considered to be important for the metabolic function of the cornea and particularly appears to have an effect on the corneal temperatures which are normally elevated by contact lens use.

It is clear that a person skilled in the art can determine the exact balance of wettability, permeability, hydrophobic, mucophobic and lipophobic properties required for the specific ocular membrane being contemplated.

In a specific embodiment, the composition of the present invention may be formed by first preparing a mixture of dimethylpolysiloxane and a catalyst with an appropriate silicon hydride, e.g. methylhydrogen-polysiloxane with the catalyst. A mixture of the ester or esters with an appropriate free radical source, such as a peroxide or an azo compound, conventionally used for such purposes, is then admixed into the silicon resin mixture. This mixing is generally carried out at room temperature and atmospheric pressure.

Thereafter, the composition is placed in an appropriate ophthalmic mould, and the final mixture is subjected to polymerization conditions to form the desired copolymeric or terpolymeric product. Typically, such polymerization conditions are from 40° to 90°C, more preferably from 65° to 85°C, for a time perod of from 30 minutes to twelve hours, more preferably from four to eight hours.

The mixture may also be postcured. Such postcuring may or may not be carried out as desired depending on the final properties required and the specific components used. Generally, postcuring is carried out at a temperature from 100°C. to 150°C, more preferably from 120°C. to 140°C, for a time period of from one to six hours. Such postcuring is generally desirable to eliminate any traces of the free radical source as well as to ensure complete cross-linking of the composition.

In a preferred method of preparation, the ester compound includes 2-hydroxypropylmethacrylate (sometimes referred to herein as propylene glycol monomethacrylate) which is first prepolymerized, either alone or mixed with another ester if a terpolymer is to be prepared, in the presence of a catalyst, e.g. azobis isobutyronitril , in an amount, such as about 0.1% by weight, at a temperature of less than about 9°C. for less than about 60 minutes. This may b further mixed with water in an amount up to 20% by weight of the 2-hydroxypropylmethacrylate. This prepolymer may then be added to the polysiloxane and mixed for about 10 minut s or less. An appropriate amount of the hydrogen siloxane needed for the cross-linking along with a chlorplatinic acid derivative catalyst ar then added to complete the casting mixture.

Mor particularly, the copolymeric composition is prepared by mixing 0.01 to 0.06 parts by weight, more preferably from 0.02 to 0.05 parts by weight, of an appropriate free radical source with from 0.3 to 3.0 parts by weight (based on the final weight of the elastomer to be prepared), more preferably from 0.5 to 2.0 parts by w ight, of the appropriate ester.

The free radical sources are generally peroxides, since they are the most readily available. The specific free radical source used is not critical, so long as it effectively produces a source of the desired free radicals. A pr ferred source is one which would be effective at a moderate temperature of 50° to 90°C. Typically, organic peroxides, such as benzoyl peroxide, acetyl peroxide, lauroyl peroxide, decanoyl peroxide and capryl peroxide, can be used.

The mixing of the ester and the peroxide is carried out by agitation and is not particularly critical. The mixing of the ester and the peroxide may be generally carried out at about room temperature.

An appropriate polysiloxane mixture is then prepared, for example by adding one to twenty-five parts by weight, more preferably five to twenty parts by weight of methylhydrogenpolysiloxane to about one hundred parts by weight of the resin, i.e. the dimethylpolysiloxane.

This mixing can also be carried out at about room temperature and the speed of mixing is not particularly critical.

The first and second mixtures are then added to one another and mixed by agitation. This final mixture may then be degassed by applying a vacuum to remove any air bubbles.

If desired, prior to subjecting the mixture to the final polymerization conditions, it is possible to add conventional additives, such as pigments. Typical pigments used in the optical field include organic pigments, such as dioxazione, napthol, and aluminium lakes, and various inorganic pigments, such as titanium dioxide, hydrated chrome, and ultramarine blue. Obviously, any colouring pigment utilized must be non-toxic and must remain stable in the presence of the oxidizing agent utilized in the polymerization. Typicaly, for example, 0.0001 to 0.01 parts by weight of a pigment will be used, depending upon the desired depth and shade of the colour.

Also, known reinforcing fillers, e.g. fine silica, may be used in compositions of the present invention in amounts which do not detrimentally affect the desired properties. From 1% to 50% by weight, more preferably 2% to 9% by weight, of such filler, based on the weight of the polysiloxane, may be used.

The finished polymer composition does not retain more than about 10% by weight of water. However, its surface possesses adequate wettability so as to provide a continuous tear or aqueous film in the manner as discussed herein. Moreover, the composition exhibits lipophobic and mucophobic properties as well as an ability to resist dust collection.

Additionally, this final polymer composition is highly permeable to oxygen and carbon dioxide, but is inert, non-toxic and completely compatible with the human eye. Moreover, being hydrophobic, it does not swell with water and can be made to conform closely and naturally to the most intricate ocular topography. It possesses a stable index of refraction under all required conditions and is durable, flexible and transparent. Moreover, it does not support bacterial growth and is ideally suited for making the disposable ocular membranes of the present invention.

Referring to the drawings, Figure 1 is a plan view of an ocular membrane formed from a composition of the present invention, while Figures 2, 3 and 4 show cross-sectional views of ocular membranes formed from the composition of the present invention. Of course, the specific shape of the membrane itself will depend upon the specific ophthalmic prescription required.

Figures 1 and 2 show a planar membrane 10 having an anterior surface 12, a posterior surface 14, and a pupillary zone 16 and an extrapupillary zone 18 disposed about the central axis 20 of the membrane. The anterior surface meets the posterior surface at the edge 22 of the membrane in a manner to be more fully described below.

Figure 3 shows a plus power membrane 24 having an extrapupillary zone 26, a pupillary zone 28 of a converging miniscus type, the anterior surface 30 of the pupillary zone having a shorter radius of curvature than the posterior surface 32 of the pupillary zone. The edge 34 of the membrane is formed in the same manner as that of the membrane shown in Figure 2 and Figure 4 as described below.

Figures 4 and 5 show a minus power membrane 36 positioned on a human eye 38 partially beneath on eyelid 40. The pupillary zone 41 of the membrane 36 is a minus powered miniscus the anterior surface 42 of which has a larger radius of curvature than the posterior surface 44 thereof.

The extrapupillary zone 46 of the membrane 36 terminates at an edge 48 which is formed by the intersecting edge curve on the anterior periphery of the membrane which intersects with the uniformly curved extrapupillary surface of the posterior surface.

The edges of the other ocular membranes also terminate in this manner which is most clearly shown in Figure 8, where the intersecting curve R_3 is formed on the anterior periphery of an ocular membrane having a radius of curvature R_2, and R_3 intersects the uniformly curved extrapupillary posterior surface having a radius of curvature R_1.

The important aspect of an ocular membrane of the present invention insofar as its physical form is concerned is that fact that it can be made extremely thin. Because of this thinness and the resultant lightness and permeability of the material to oxygen and carbon dioxide, the membrane may simply be placed on the eye in the usual manner and may b retained there for a number of days, weeks and even months without adverse ffects on the eye. Additionally, the thinness of the membrane coupled with the elasticity of the composition makes the membrane extremely flexible so that it is deformable by pressure of the eyelid during the normal blinking cycle. This deformation enhances circulation of the precorneal fluid, further improving the metabolic compatibility of the membrane with the eye. Of course, the period of time that a given ocular m mbrane can be worn will depend to a great extent on the wearer and the ophthalmic

prescription involved. However, it is clear that the ocular membrane of the pres nt invention can, for any given wearer, be worn for significantly greater periods than the conventional contact lenses presently known.

As seen near the periphery of the membrane 36, a wrinkle or local temporary deformation 50 is produced during the blinking cycle. This wrinkle can be compared to a wave effect on the extrapupillary surface. The wrinkle literally produces a pumping action circulating corneal liquid from beyond the periphery of the membrane to and from under the membrane in order to enhance the metabolic compatibility of the membrane with the eye.

Additionally, because the extrapupillary zone of the membrane is so thin, deformation produced by the blinking process is restricted to the extrapupillary section and does not in any way produce deformations in the pupillary zone of the membrane which would result in visual distortions to the wearer of the membrane. This is made possible because the relative thinness of the extrapupillary section produces a relatively greater flexibility in the extrapupillary section than in the pupillary section of the membrane.

The present composition, after curing, has a light transmission as required for optical use, i.e. as measured by a spectrophotometer of better than eight-five per cent on a one mil thick sample, although for certain uses light transmissions as low as 80 per cent might be allowable.

The ocular membrane of the present invention is prepared by first forming a lens mould cavity composed of two mould members, a concave member and a convex member. The convex member is a replica of the ocular surface with a small pupillary segment conforming in its geometry to the topography of the human cornea. Of course, the pupillary segment in the concave member of the mould would conform to the specifications of the ophthalmic prescription.

The mould members are made from plastics materials which are soluble in solvents in which the lens copolymer is not soluble. Examples of suitable materials which can be used as the mould members include polymethylmethacrylate, ethyl cellulose, cellulose acetate, polystyrene, vinyl acetate, epoxy resin, methyl cellulose acetate, acrylic butadiene styrene copolymer and caranuba wax.

A die for forming the mold members is first made. The die can be made from a calcium sulphate impression which, utilizing conventional methods, is formed by making an impression of the human eye or, alternatively, an impression of a life-size model of the human eye. The die is generaly made of a metal, e.g. steel, chrome, or nickel.

An impression may be made of the entire sclera and cornea; a part of the sclera and all of the cornea; or alternatively only of the cornea itself, in whole or in part. Whichever impression is made, it is of course ultimately transferred to the final ocular membrane. Thus, depending upon the particular prescription, the ocular membrane will cover either the entire sclera and all of the cornea, or only part of the sclera and all of the cornea, or only cover the cornea, in whole or in part. The convex mould will possess a configuration identical to the concave mould with the exception of a central pupillary area which possesses geometry and dimensions as dictated by the specific refractive ophthalmic prescription being used. In addition, the concave mould is so shaped as to permit it and the convex mould to meet uniformly over the entire perimeter of the two moulds when brought together.

Thermoplastics moulds are made by conventional casting, injection moulding, or compression moulding methods utilizing metallic master dies, as previously mentioned. They may be formed from calcium sulphate impressions of the eye or, alternatively, machined to duplicate standardized models of the human eye topography over the entire range thereof. This procedure permits perfect duplication of either unique models or standard models of ocular topography through the use of various plastics materials.

The relationship between the moulds and membrane is shown in Figures 6 to 8, and the method by which the moulds are used to form the membrane is shown in Figures 9 to 12.

In Figure 6, a mould assembly 52 has a convex mould 54 positioned above a concave mould 56. The concave mould 56 has a central pupillary portion 64 and has a raised circumferential annular surface 57 of radius of curvature R_3 as shown in Figure 7, which forms an edge 58 on a membrane 59 by intersecting with the radius of curvature R_1 of the convex mould surface because the circumferential annular surface 57 has a greater radius of curvature than the radius of curvature of the convex mould surface.

The membrane 59 is shown positioned between the upper convex mould 54 and the lower concave mould 56. The alignment of the upper convex mould 54 with the lower concave mould 56 is determined by means of the circumferential annular surface 57 of radius of curvature R_3 on the lower mould which coacts with the radius of curvature R_1 of the convex surface of the upper mould. The difference between the radius of curvature of the circumferential annular surface 57 and the radius of curvature R_1 of the convex mould surface produces the peripheral edge 58 of the membrane 59. The pupillary section 60 of the lens will be accurately positioned with relation to the peripheral edges of the membrane as long as the upper and lower mould sections are in parallel and perpendicular alignment. This is accomplished in a manner well known in the art in which the lower mould member is allowed to slide freely on a horizontal plane so that it will automatically position itself when the upper mould member engages it.

As shown in Figure 9, the first step in the formation of the ocular membrane is to properly position the convex and concave moulds 54 and 56 respectively in vertical and horizontal alignment. Then, a liquid polymer composition 68 as described hereinabove is poured from a pouring spout 66 to fill the concave mould to a level sufficient to take up the entire volume that will form th membrane. The upper mould 54 is then lowered onto the lower mould to engage the lower mould and thereby form a substantially closed

mould chamber and to expel any excess polymer liquid which has been deposited in the lower mould.

The mould halves are then left in their engaged position for a period of time sufficient for cross-linking to take place. Once this has occurred, because of the relative thinness of the ocular membrane and its intimate contact with the mould surfaces, it would be difficult if not impossible to separate the mould surfaces and remove the ocular membrane without in some way impairing the optical finish of the finished membrane.

The method of the present invention provides a membrane which, after curing, requires no further treatment in terms of finishing of edges, or removal of any end portions present due to unsealed portions of the moulds. From an economic point of view this is very important since the requirements normally associated with finishing ophthalmic devices, membranes, bandages, and lenses are a significant factor in determining the ultimate cost to the user.

Therefore, it is preferably, in order to avoid this step of removing the membrane from the mould surfaces, to remove the mould from the membrane by a destruction process in which the material from which the mould is fabricated is placed in contact with another material which is incompatible with the survival of the mould material but which will have no permanent effect on the material forming the ocular membrane. This process is shown in Figures 11 and 12, where the mould assembly 52 is positioned in a vessel 72 filled with, for example, a solvent 80 in which the mould material will dissolve but which will not in any way absorb or attack the material from which the ocular membrane is produced. After a sufficient period of time, the mould will be reduced to debris 74 shown in Figure 12 and the membrane 59 will itself float freely in the liquid. Of course, the membrane can also be removed by manual techniques.

After the membrane has floated free, it can then be removed, washed and dried and further postcuring can be accomplished if desired. Washing is generally done in a sodium chloride solution (preferably a three per cent sodium chloride solution).

It should be noted that the membrane, once released from the mould, is in the finished state and that no further forming process is necessary in order to produce any optical properties of the membrane or to impart any edge, shape or configuration to the lens.

In accordance with one embodiment of the present invention, the removal of the cured ocular membrane from the mould members is accomplished by inserting or submerging the entire mould assembly into a solvent for the mould members. As mentioned above, this solvent should be a non-solvent for the cured contact lens or ocular membrane composition but should be a good solvent for the mould material.

The following table sets forth a number of suitable plastics materials which can be used to make the mould and solvents which can be used in conjunction with them.

Mould Material	Solvent
polymethylmethacrylate	acetone
polyacrylic resin (soluble)	isopropanol
ethyl cellulose	ethyl alcohol
cellulose acetate	methyl ethyl ketone
polystyrene	toluene
vinyl acetate	methyl alcohol
epoxy resin	isophorone
methyl cellulose acetate	water
acrylic butadiene styrene	methyl ethyl ketone
caranuba wax	benzene

The minimal thickness of the ocular membrane of the present invention adds to its permeability to oxygen and carbon dioxide, thereby allowing proper metabolic functioning of the eye. In particular, the membrane produced in accordance with the present invention may be as thin as about 0.10 mm. except for a pupillary portion which performs a refractive function and whose anterior and posterior radii of curvature are determined by the required focal length as dictated by the ophthalmic presciption.

Generally, a membrane made in accordance with the present invention has a stable refractive index of 1.409 under accepted standard conditions.

The preferred characteristics of the composition and ocular membrane of the present invention are set forth below as are the methods by which they were determined:

Property	ASTM Test method	Range	Median
Hardness, Shore A Durometer	D7.85	15-95	32
Specific Gravity	D1505	0,95-1.04	1.02
Tensile Strength, psi	D 882	100-1,000	800-925
Elongation, %	D 882	120-250	150
Tearing Strength, lb	D1004	10-30	25
Water Absorption, %*	D 570	0-3	0.5

*The water absorption of the material was determined by immersing a specimen which was one-eighth inch thick in a saline solution at 80°F. The specimen was allowed to remain for two weeks and the weight increment was measured. The weight increment was found not to exceed 0.12% of the one-eighth inch specimen.

Permeability to gas
(Std cc) (cm thickness)
(Seconds) (s of cm area) (cm Hg pressure drop)

O_2 permeability	D1434	$(29\text{-}62)\times10^{-9}$	59×10^{-9}
CO_2 permeability	D1434	$(180\text{-}315)\times10^{-9}$	300×100^{-9}
Index of Refraction	D 542	1.390-1.50	1.409±0.01

The above properties compare favourably with those of the unmodified silicone elastomer, e.g. a commercially available dimethylpolysiloxane/methyl hydrogen siloxane system (DMPS). However, the compositions of the present invention possess important properties as set out below which make them particularly suitable for use in ocular membranes, which properties are not possessed by the conventional DMPS.

	Compositions of present invention	DMPS
wetting angle	20°30°	60°40°
lipophobia	good	none
mucophobia	good	none

The relative proportions of the ester and polysiloxane in the final product will vary depending on the particular materials used and final properties desired. Typically, for example, when the ester used is 2-hydroxypropylmethacrylate, it is preferably employed in an amount of 0.1 to 5 per cent by weight, more preferably 0.5 to 2 per cent by weight.

The upper limit in this instance is important from the standpoint of light transmission. Thus, at 2-hydroxypropylmethacrylate amounts of more than about 5 per cent by weight, the light transmission is reduced to less than about 79 per cent, which makes such material less suitable as an optical material. Conversely, at least about 0.1 per cent is required to produce the desired properties of wettability, lipophobia, and mucophobia. Clearly, for a given choice of materials, the amount of the ester should be that amount effective to produce at least about 80% light transmission as well as maintain the desired levels of lipophobia, wettability, mucophobia and minimal dust affinity.

For the above measurements, the wetting angle was measured by the Poster inverted air bubble method. This is a simulated *in vivo* method carried out on flat samples which were soaked for seven days in normal saline. The specific procedure used is as outlined in *International Contact Lens Clinic,* Vol. 5 No. 1, January-February 1978.

Lipophobia was determined in an emulsion of 93% normal saline, 5% vegetable oil and 2% starch. Full hydrated samples were immersed for 30 seconds, withdrawn from the emulsion and washed in normal saline for 30 seconds. The integrity of the water film was observed visually.

Mucophobia was determined by empirical observation of samples of membranes placed on the corneas of rabbits for 21 days. The samples were fully hydrated prior to insertion. Full hydration was achieved after 48 hours of immersion in an aqueous medium.

The following table shows the effects of varying amounts of the esters 2-hydroxypropylmethacrylate (2-HPMA) in the composition according to the invention:

Formulation Siloxane Weight %	2-HMPA	Immersion time Needed to achieve Full hydration	Rejection of mucus, Lipids and Particulate debris
100	0	14 days	poor
99.9	0.1	7 days	fair
99.8	0.2	48 hrs.	good
99.5	0.5	29 hrs.	good
99.0	1.0	12-18 hrs.	good
98.0	2.0	12-18 hrs.	good
97.0	3.0	12-18 hrs.	good
95.0	5.0	12-18 hrs.	excellent

By "full hydration", there is meant that a continuous uninterrupted film of liquid (normal saline) may be established on the surface of the material. The establishment of such a film may be determined by visual observation. The property is inherently associated with the "wettability" of the film and is essentially another parameter which can be used to characterize the suitability of the material for use as an ocular membrane in contact with the eye.

The importance of this property is that once full hydration has been obtained, a continuous uninterrupted film is established and the membrane may be exposed to the air at ambient temperatures and the integrity of the film will be sustained for varying lengths of time. The following table shows the effect of variations in composition on the length of time for which the film will be maintained (after full hydration):

	Formation Polysiloxane	2-HPMA	Duration of film
a.	100	0	20- 50 minutes
b.	99.9	0.1	35- 65 minutes
c.	99.8	0.2	120-150 minutes
d.	99.5	0.5	140-180 minutes
e.	99.0	1.0	160-180 seconds
f.	98.0	2.0	160-180 seconds
g.	97.0	3.0	160-180 seconds
h.	95.0	5.0	150-180 seconds

In use, ocular membranes according to the present invention in contact with the eye will be in an environment of aqueous corneal fluid. Thus, the film established at full hydration is ensured. When blinking, the lid interrupts and re-wets the anterior surface of the membrane with corneal fluid. At a minimal blink rate of 2 to blink per minute, an ocular membrane in accordance with the present invention maintains a continuous film at all times. However, since the corneal fluid contains the lipid and mucous debris, the continuous wetting and re-wetting of the surface of the membrane provides ample opportunity for the debris to collect on and adhere to the membrane, depending on the affinity of the membrane material for the debris.

It is thus important that the surface of the material not only wets, i.e. attracts water, but also rejects the lipid and mucous debris. Otherwise the membrane will become coated with the debris and this will result in reduced transmission and lower visual acuity.

To evaluate the effect of the composition of the present invention on the lipophobic and mucophobic properties of membranes, the following experiment was carried out.

An emulsion to simulate the corneal fluid (loaded with mucous and lipids) was prepared by mixing 2 per cent by weight starch, 3 percent by weight vegetable oil and 95 per cent saline (0.9N NaCl) thoroughly for 30 minutes in a Waring blender.

Fully hydrated membranes were immersed in the emulsion for 30 seconds, immersed in distilled water for 30 seconds and then visually evaluated for the presence of an uninterrupted continuous film of water. The results were as follows:

	Copolymer 2-HMPA	Formulation DMPS$_{RTV}$	Surface Hydrophilic	Surface Lipophilic	Surface Mucophobic
(a)	0.0	100.0	poor	excellent	excellent
(b)	0.1	99.9	fair	very good	very good
(c)	0.2	99.8	good	good	good
(d)	0.3	99.7	good	fair	fair
(e)	0.5	99.5	excellent	poor	poor
(f)	1.0	99.0	excellent	poor	poor
(g)	2.0	98.0	excellent	poor	poor
(h)	3.0	97.0	excellent	poor	poor
(i)	5.0	95.0	excellent	poor	poor

The invention will be further described with reference to the following illustrative Examples.

Examples 1-13

In these examples, flat films of copolymers and terpolymers in accordance with the present invention were prepared using varying amounts of the esters as indicated. The films were prepared by first preparing the polysiloxane. This was prepared by mixing 10 grams of dimethylpolysiloxane having about 0.25 per cent of the methyl groups replaced by vinyl groups and 1.5 grams of methyl hydrogen siloxane containing a catalytic amount of chlorplatinic acid alcoholate. 11.5 Grams of this mixture were mixed with the ester or esters indicated to which 3 per cent by weight of butyl octoate as a catalyst was added. The mixture was agitated for 10 minutes in a rotary mixer at 1250 r.p.m. and then permitted to de-air at ambient temperature for one hour.

Films were prepared from these mixtures by delivering 0.16 grams of the mixture at ambient temperature onto a level polished polymethylmethacrylate plate using a polymethyl pentene syringe having a 2.0 mm opening. The plate was placed in an air circulating oven at 90°C to completely cure the sample. Depending on the composition used, the curing time varied from 40 minutes to 8 hours.

The thus formed film (or flat) having a thickness of about 1 mm was cut into 4 mm × 16 mm strips and analyzed for light transmittance, wetting properties, elongation and antistatic properties. Not all of the samples were analyzed for each property. The analyses were carried out as follows:

Light transmission:

The sample was placed in a 0.5 mm square curvette in a 0.9% saline (normal saline). The transmission was measured against normal saline solution using a Lumitron 15 Photocolorimeter, Photovolt, Inc.

Wetting:

The sample was immersed in normal saline for 24 hours. The sample was removed and held in a vertical position and the elapsed time of duration of the integrity of the aqueous film on the sample was measured. Six determinations were made for each sample at ambient temperature (63°F) at 35 to 40 per cent humidity, and the average of the six determinations was used.

The characterization of the duration time of the film was as follows:

90 seconds or more	=	excellent
60 to 89 seconds	=	good
40 to 59 seconds	=	fair
less than 40 seconds	=	poor

Elongation:

The sample was elongated at constant force until it broke. The increase in length until breaking was noted in terms of percentage of original length.

Antistatic properties:

This was a qualitative test to characterize the antistatic properties of the flat sample. Finely powdered cigar ash was placed on a dry, flat sample to completely cover the surface of the sample. The ash was then blow off using a 60 second compressed (50 psi) air blast through a $\frac{1}{8}$ inch nozzle placed half inch from the sample. The amount of ash remaining on the surfac was measured by usin a 0.01 mm grid under 20× magnification. The results were characterized as follows:

per cent of grid squares remaining covered	
2% or less	excellent
2 to 5%	very good
5 to 7%	good
7 to 10%	fair
more than 10%	poor

Water Absorbtion:

The sample was immersed in normal saline at ambient temperature (77°F). The increment in weight after one week of immersion was measured.

The results obtained were as follows.

EXAMPLE 1

Copolymer of dimethylpolysiloxane with propylene gycol monomethacrylate.

Amount of ester, Wt%	Light Trans.,%	Elongation, %	Wetting	Antistatic	H_2O Absorbtion,%
0.2	90				
0.5	90				
1.0	88	35	excellent	excellent	0.5
2.0	light haze	25			
3.0	haze, opaque				0.7

Note: Curing inhibited on steel alloys.

EXAMPLE 2

Copolymer of dimethylpolysiloxane with 1,4 butylene glycol monomethacrylate.

Amount of ester, Wt %	Light Trans., %	Elongation,%	Wetting	Antistatic	H_2O absorbtion, %
0.2	over 90		poor		
0.5	over 90		fair		
1.0	over 90		good		
2.0		60	excellent	good	
3.0			excellent		
4.0			excellent		
5.0			excellent		
7.5	86		excellent		

EXAMPLE 3

Copolymer of dimethylpolysiloxane with hexamethylene glycol diacrylate.

Amount of ester, Wt %	Light Trans., %	Elongation, %	Wetting	Antistatic	H_2O absorbtion
0.2			poor		
0.5			poor		
1.0	89		good		good
2.0	89		fair		fair
3.0	89		good		fair
4.0	85		good		good
5.0	70		good		
7.5	opaque				

EXAMPLE 4

Copolymer of dimethylpolysiloxane with hexamethylene glycol dimethacrylate.

Amount of ester, Wt %	Light Trans., %	Elongation, %	Wetting	Antistatic	H_2O absorbtion, %
0.2			poor		
0.5			poor	fair	
1.0	88		excellent		
2.0	clear				
3.0	clear		excellent	good	
4.0	clear		excellent		
5.0	clear		good	poor	
6.0	clear		good		
7.5	clear		good		
10.0	clear		excellent		

EXAMPLE 5

Copolymer of dimethylpolysiloxane with 2-methoxyethylmethacrylate.

Amount of Ester, Wt %	Light Trans., %	Elongation, %	Wetting	Antistatic	H_2O absorbtion, %
0.2			poor	poor	
0.5			poor	poor	
1.0	90	50	good		0.7
2.0					
3.0					
4.0					
5.0					
7.5			poor	poor	

EXAMPLE 6

Copolymer of dimethylpolysiloxane with 2-methoxyethylacrylate

Amount of ester, Wt %	Light Trans., %	Elongation, %	Wetting	Antistatic	H_2O absorbtion, %
0.2	91		fair	fair	
0.5	91		fair	fair	
1.0	91		good		0.8
2.0	91		fair		
3.0	91		fair		
4.0	91		fair		
5.0	91		poor		
7.5	91		good		
12.5	91		good		

EXAMPLE 7

Copolymer of dimethylpolysiloxane with tetramethylene glycol diacrylate.

Amount of ester, Wt %	Light Trans., %	Elongation, %	Wetting	Antistatic	H_2O absorbtion, %
0.2	90		fair		
0.5	90		fair		
1.0	90		good		
2.0	90		good		
3.0	88		excellent		
4.0	85				

EXAMPLE 8

Copolymer of dimethylpolysiloxane with tetramethylene glycol dimethacrylate

Amount of ester, Wt %	Light Trans., %	Elongation, %	Wetting	Antistatic	H_2O absorbtion, %
0.2			poor	poor	
0.5		fair			
1.0	90		good	good	
2.0			good	excellent	
3.0	90		good		
4.0			excellent		
5.0			excellent		

EXAMPLE 9

Copolymer of dimethylpolysiloxane with neopentyl glycol diacrylate.

Amount of ester, Wt %	*Light trans., %*	*Elongation, %*	*Wetting*	*Antistatic*	*H_2O absorbtion, %*
0.2	*90*		*poor*	*poor*	
0.5	*90*		*poor*	*poor*	
1.0	*90*		*fair-poor*	*fair*	
2.0	*90*		*excellent*	*good*	
3.0	*89*		*excellent*	*good*	
4.0	*89*		*excellent*	*good*	
5.0	*88*		*excellent*	*good*	
7.5	*slight haze*		*excellent*	*good*	

EXAMPLE 10

Copolymer of dimethylpolysiloxane with neopentyl glycol methacrylate

Amount of ester, Wt %	Light trans., %	Elongation, %	Wetting	Antistatic	H_2O absorbtion, %
0.2	clear			poor	
0.5	90			poor	
1.0	90		poor	fair	
2.0	90		fair	good	
3.0	90		fair	good	
4.0	90		fair	good	
5.0	90		excellent	good	
7.5	90			good	
10.0	90			good	

EXAMPLE 11

Terpolymer of dimethylpolysiloxane with ester I, 2-hydroxypropylmethacrylate, and ester II, tetramethylene glycol dimethacrylate

Amount of ester, Wt %		Light trans., %	Elongation, %	Wetting	Antistatic	H_2O absorbtion, %
I	*II*					
0.5	0.5	90	45	fair		
1.0	1.0	90	40	good		
2.0	1.0	90	40	good		
1.0	2.0	90	40	good		
3.0	1.0	haze				

Note: Curing inhibited by steel dies.

EXAMPLE 12

Terpolymer of dimethylpolysiloxane with ester I, 2-hydroxypropylmethacrylate, and ester II, tetramethylene glycol diacrylate

Amount of ester, Wt %		Light trans., %	Elongation, %	Wetting	Antistatic	H_2O absorbtion, %
I	*II*					
0.5	0.5	90	40	fair		
1.0	1.0	89	38	good		
2.0	1.0	88	38	good		
1.0	2.0	haze				
3.0	1.0	haze				

EXAMPLE 13

Terpolymer of dimethylpolysiloxane with ester I, 2-hydroxypropylmethacrylate, and ester II, 2-methoxyethylacrylate

Amount of ester, Wt %		Light trans., %	Elongation, %	Wetting	Antistatic	H_2O absorbtion, %
I	*II*					
0.5	0.5	91	50	good	good	
1.0	1.0	91	48	good		
2.0	1.0	91	45	good		
1.0	2.0	90	45	good		
3.0	2.0	slight haz	40	good		
2.0	3.0	86	40	good		

Membranes from each of the copolymers and terpolymers described in Table 2 below were prepared by placing the specified mixture into a closed cell formed by marrying two mould members made of polyacrylic resin (Carboset XLII-B.F. Goodrich) having the desired optical geometry. The mixtures and components were prepared in the same manner as for the flat samples. The mixture in the closed cell was cured using the conditions described above for the preparation of the films. After curing, the moulds were destroyed by dissolution in isopropanol, thus freeing the membranes.

The thus obtained membranes were clinically tested on humans with continuous periods of wear ranging from 24 to 72 hours. The membranes exhibited good optical definition, good mucophobicity and lipophobicity which resulted in satisfactory levels of visual acuity over the entire wearing period; the lenses were tolerated well by the wearers and no corneal injury was observed.

Membrane 20 was tested on rabbits for six weeks and no corneal injury was observed.

TABLE 2

Ester components of membranes

Membrane No.	Comments	Ester No. (from Table 1)	% Weight
1		9	1.0
2		10	1.0
3	terpolymer	7	1.0
		1	1.0
4	terpolymer	6	3.5
		1	1.0
5		6	5.0
6		6	4.0
7		6	3.0
8		6	2.0
9		6	7.0
10		6	3.0
11		6	1.0
12		1	1.0
13		1	1.0
14		1	1.0
15	terpolymer	1	1.0
		7	1.0
16		7	1.0
17		3	1.0
18		4	1.0
19		5	1.0
20		1	1.0

TABLE 2 (cont...)

Membrane No.	Comments	Ester No. (from Table 1)	% Weight
21	terpolymer	6	1.0
		1	1.0
22		6	1.0
23	terpolymer	1	1.0
		8	1.0
24		8	1.0
25		10	2.0
26		9	2.0
27		10	3.0

CLAIMS

1. A composition comprising a uniform polymer selected from copolymers and terpolymers of an addition cross-linked polysiloxane and one or more esters having the formula:

$$A-\overset{\overset{\displaystyle O}{\|}}{C}-O(CR'_2)_x-\Big[\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}\Big]_y-(CR'_2)_zO-R \qquad (I)$$

wherein:

A is $CH_2{=}CH-$ or $CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}-$,
R' may be the same or different in each occurrence and is hydrogen or methyl,
R is hydrogen, an alkyl group having on to three carbon atoms,
$CH_2{=}CH-\overset{\overset{\displaystyle O}{\|}}{C}-$, or $CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}$,
x and z are each integers from 0 to 4,
y is 0 or 1,

the sum of x and z is one or more, and when y is 1 x and z are equal,

the amount of the ester in the polymer being effective to provide the composition with sufficient light transmission, liphobicity, mucophobicity, and surface wettability, for wearing in contact with the human eye but less than that which would make the composition water swellable.

2. A composition as claimed in Claim 1, further comprising a reinforcing filler in an amount of from 1 to 50 per cent by weight of the polysiloxane.

3. A composition as claimed in Claim 2, wherein the reinforcing filler is present in an amount of from 2 to 9 per cent by weight of the polysiloxane.

4. A composition as claimed in any of Claims 1 to 3, having a refractive index of from 1.390 to 1.500.

5. A composition as claimed in any of Claims 1 to 4, wherein the amount of the said ester is from 0.2 to 5 per cent by weight based on the total weight of the polymer.

6. A composition as claimed in any of Claims 1 to 5, wherein the polysiloxane is dimethylpolysiloxane.

7. A composition as claimed in Claim 6, wherein the polysiloxane is dimethylpolysiloxane having up to about 1 per cent of the methyl groups replaced by vinyl groups.

8. A composition as claimed in any of Claims 1 to 7, wherein the ester is a mono ester.

9. A composition as claimed in any of Claims 1 to 7, wherein the ester is a diester.

10. A composition as claim d in any of Claims 1 to 7, wherein the ester is a mixture of mono and diesters.

11. A composition as claimed in any of Claims 1 to 7, wherein the ester is selected from propylene glycol monomethacrylate, 1,4 butylene glycol monomethacrylate, hexamethylene glycol dimethacrylate, hexamethylene glycol diacrylate, 2-methoxy ethylacrylate, 2-methoxy ethyl methacrylate, tetramethylene glycol dimethacrylate, tetramethylene glycol diacrylate, neopentyl glycol diacrylate, and neopentyl glycol

dimethacrylate.

12. A composition as claimed in any of Claims 1 to 7, which is a terpolymer consisting essentially of one per cent by weight of propylene glycol monomethacrylate, one per cent by weight of 2-methoxyethylacrylate and 98 per c nt by weight of dimethylpolysiloxane.

13. A composition as claimed in any of Claims 1 to 7, which is a copolymer wherein the ester is 2-methoxyethylacrylate in an amount of about 1.12 per cent by weight.

14. A composition as claimed in any of Claims 1 to 7, which is a terpolymer wherein the esters comprise about 1.0 per cent by weight of propylene glycol monomethacrylate and about 1.0 per cent by weight of tetramethylene glycol diacrylate.

15. A composition as claimed in any of Claims 1 to 7, which is a copolymer wherein the ester is 1, 4 butylene glycol monomethacrylate in an amount from 1 to 4 per cent by weight.

16. A composition as claimed in any of Claims 1 to 7, which is a copolymer wherein the ester is neopentyl glycol dimethacrylate in an amount of about 3 per cent by weight.

17. A composition as claimed in any of Claims 1 to 7, which is a copolymer of addition cross-linked dimethylpolysiloxane and propylene glycol monomethacrylate, the amount of propylene glycol monomethacrylate being from 0.5 to 2 per cent by weight based on the total weight of the copolymer.

18. A composition as claimed in any of Claims 1 to 7, which is a uniform terpolymer of addition cross-linked dimethylpolysiloxane and two esters having the formula (I) as defined in Claim 1, wherein one of the esters is propylene glycol monomethacrylate, the total amount of the two esters being effective to provide the composition with sufficient light transmission, liphobicity, mucophobicity, and surface wettability, for wearing in contact with the human eye but less than that which would make the composition water swellable.

19. A composition as claimed in Claim 18, wherein the amount of the esters is from 0.2 to 5 per cent by weight based on the total weight of the terpolymer.

20. A composition according to Claim 1, substantially as herein described in any of the foregoing Examples.

21. An ocular membrane formed from a composition as claimed in any of Claims 1 to 20.

22. An ocular membrane as claimed in Claim 21, having an average extrapupillary thickness of less than 0.05 to 0.20 mm.

23. An ocular membrane according to Claim 21, substantially as herein described with reference to, and as shown in, the accompanying drawings.

24. A method of forming an ocular membrane, comprising forming ophthalmically contoured concave and convex mould members adapted to mutually engage along a continuous closed loop; introducing into the said concave mould member a polymerizable material comprising an addition cross-linkable polysiloxane and one or more esters having the formula:

$$A{-}\overset{O}{\overset{\|}{C}}{-}O\,(CR'_2)_x{-}\left[\,\underset{CH_3}{\overset{CH_3}{C}}\,\right]_y{-}(CR'_2)_zO{-}R \qquad (I)$$

wherein:

A is $CH_2{=}CH{-}$ or $CH_2{=}\overset{CH_3}{C}{-}$,
R' may be the same or different in each occurrence and is hydrogen or methyl,
R is hydrogen, an alkyl group having one to three carbon atoms,
$CH_2{=}CH{-}\overset{O}{C}{-}$, or $CH_2{-}\overset{CH_3}{C}{-}\overset{O}{C}$,
x and z are integers from 0 to 4,
y is 0 or 1,
the sum of x and z is one or more, and when y is 1 x and z are equal,

the amount of the ester in the polymer being effective to provide the composition with sufficient light transmission, liphobicity, mucophobicity, and surface wettability, for wearing in contact with the human eye but less than that which would make the composition water swellable; contacting the convex mould member with the concave mould member to expel excess polymerizable material th refrom and to form a substantially closed mould chamber having essentially the size and shape of the completed membrane; subjecting the thus-introduced polymerizable material to polymerization conditions to form a polymeric ocular membrane from the said material possessing the contours of the substantially closed mould chamber; and freeing the formed ocular membrane from the substantially closed mould chamber.

25. A method as claimed in Claim 24, wherein the freeing of the formed ocular membrane from the mould chamber includes the step of dissolving the mould members away from the membrane with a solvent in which the mould members are soluble but in which the membrane is insoluble.

26. A method as claimed in Claim 24 or 25, wherein the ester is a mono ester.

27. A method as claimed in Claim 24 or 25, wherein the ester is a diester.

28. A method as claimed in Claim 24 or 25, wherein the ester is a mixture of mono and diesters.

29. A method as claimed in Cliam 24 or 25, wherein the ester is selected from propylene glycol monomethacrylate, 1,4 butylene glycol monomethacrylate, hexamethylene glycol dimethacrylate, hexamethylene glycol diacrylate, 2-methoxy ethylacrylate, 2-methoxy ethyl methacrylate, tetramethylene glycol dimethacrylate, tetramethylene glycol diacrylate, neopentyl glycol diacrylate, and neopentyl glycol dimethacrylate.

30. A method as claimed in Claim 24 or 25, wherein the polymerizable material comprises addition cross-linked dimethylpolysiloxane and propylene glycol monomethacrylate, the amount of propylene glycol monomethacrylate being from 0.5 to 2 per cent by weight based on the total weight of the material.

31. A method as claimed in Claim 24 or 25, wherein the polymerizable material comprises dimethylpolysiloxane and two esters having the formula (I) as defined in Claim 24, wherein one of the esters is propylene glycol monomethacrylate, the total amount of the two esters being effective to provide the composition with sufficient light transmission, liphobicity, mucophobicity, and surface wettability, for wearing in contact with the human eye but less than that which would make the composition water swellable.

32. A method as claimed in Claim 31, wherein the amount of the esters is from 02 to 5 per cent by weight based on the total weight of the material.

33. A method as claimed in Claim 24 or 25, wherein the polymerizable material is a terpolymer consisting essentially of one per cent by weight of propylene glycol monomethacrylate, one per cent by weight of 2-methoxyethylacrylate and 98 per cent by weight of dimethylpolysiloxane.

34. A method according to Claim 24 of forming an ocular membrane, substantially as herein described with reference to the accompanying drawings.

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